Hydrogen in Transport: H_2, NH_3, LNG & Methanol as Future Maritime Energy Carriers

Nikos Xynopoulos

Hydrogen Industry Leaders, Manchester 2024

Contributors

- **Nikos Xynopoulos**
  Chemical Engineer | *Petroleum Engineer* | *Oil & Gas Engineer*
- **Education**
- **Aristotle University of Thessaloniki (AUTH):** MSc in Chemical Engineering
    - Major: NH3 Synthesis under Prof. Michael Stoukides
- **Technical University of Crete (TUC):** MSc in Petroleum Engineering
    - *Scholarship by Hellenic Petroleum Group SA*
- **University of Aberdeen:** Postgraduate Studies in Oil & Gas Engineering
- **Professional Experience**
- **Current:** *Plant Manager*, Linde Group
    - Managing Air Separation Units, H_2 Production Unit (Electrolyser) & Filling Station, VPSA units
- **HelleniQ Energy:** Senior Chemical Engineer & Project Manager, Digitalization Division, Refinery Marine Section
- **Motor Oil Hellas Corinth Refineries:** Gasolines & Fuels Prodcuction Complex Operations Engineer
- **Nalco Water/Ecolab:** Chemical Treatment Program Manager for all four (4) Greek refineries
    - Expertise in Boiler Water, CDU Anticorrosion, Cooling Tower Treatments
- **Ship Supply Industry:** YOKOHAMA RUBBER CO. Representantive. Region East Europe
- Technical & QC Supervisor on Ship to Ship (STS) Equipmnet for LNG, Crude Oil and Chemicals
- **Desalination Industry:** Chemical Engineer, Culligan Greece
- **Specializations**
- Hydrogen Production, LNG STS, Refinery Operations, Water Treatment

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Acknowledgment

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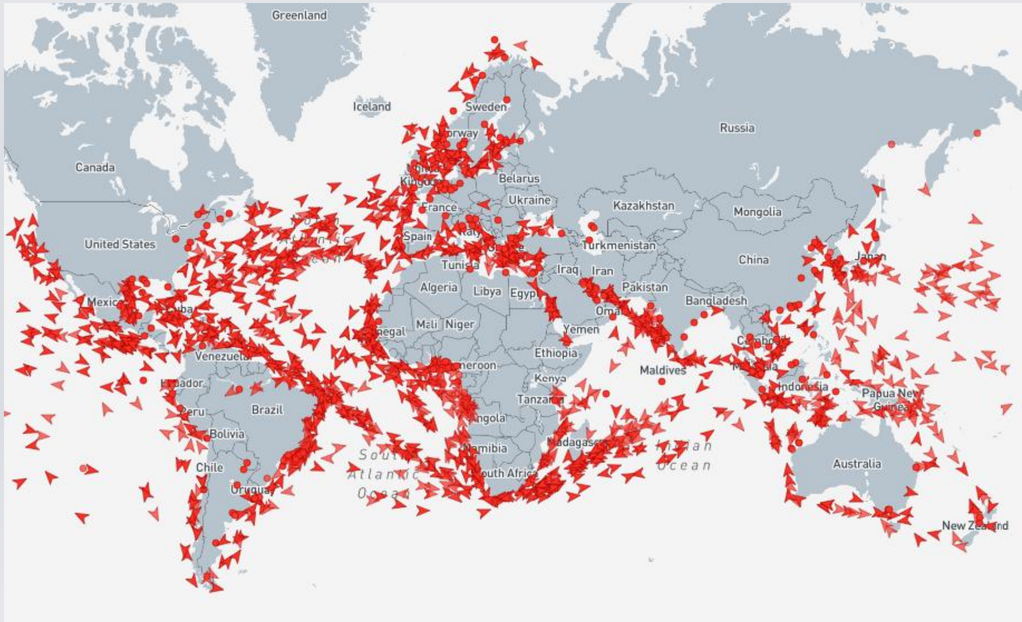
Global Fleet

- Approximately ~60.000 ships in operation
- Bulk carriers, container ships, oil tankers, LNG carriers among others
- Shipping facilitates >90% of global trade
- Air pollution accounts for 3% of CO_2 emissions & 14% of SO_2 emissions.
- 10.000 times more S than road transport
- Cumulative effect on air quality
- More than 7.000 ships have implemented compliant ship fuel equipment



Environmental Impact of Shipping

Energy mixture constantly and rapidly changes

- Greener Solutions
- Safe and Reliable
- Diverse Sources of Energy
- Economically Beneficial and Sustainable

Geopolitical Challenges

- Global population: 9.5 billion by 2030
- Fertilizers Production Demands
- Strict Legislation (ex. IMO 2020)
- Geopolitical Turmoil

Energy Market is impacted

- Industrial Gases market rise
- Need for new infrastructure
- Integration with old resources & and equipment
- Digitalization

Efficient Storage and Transportation

- Liquid Hydrogen
- LNG
- NH3

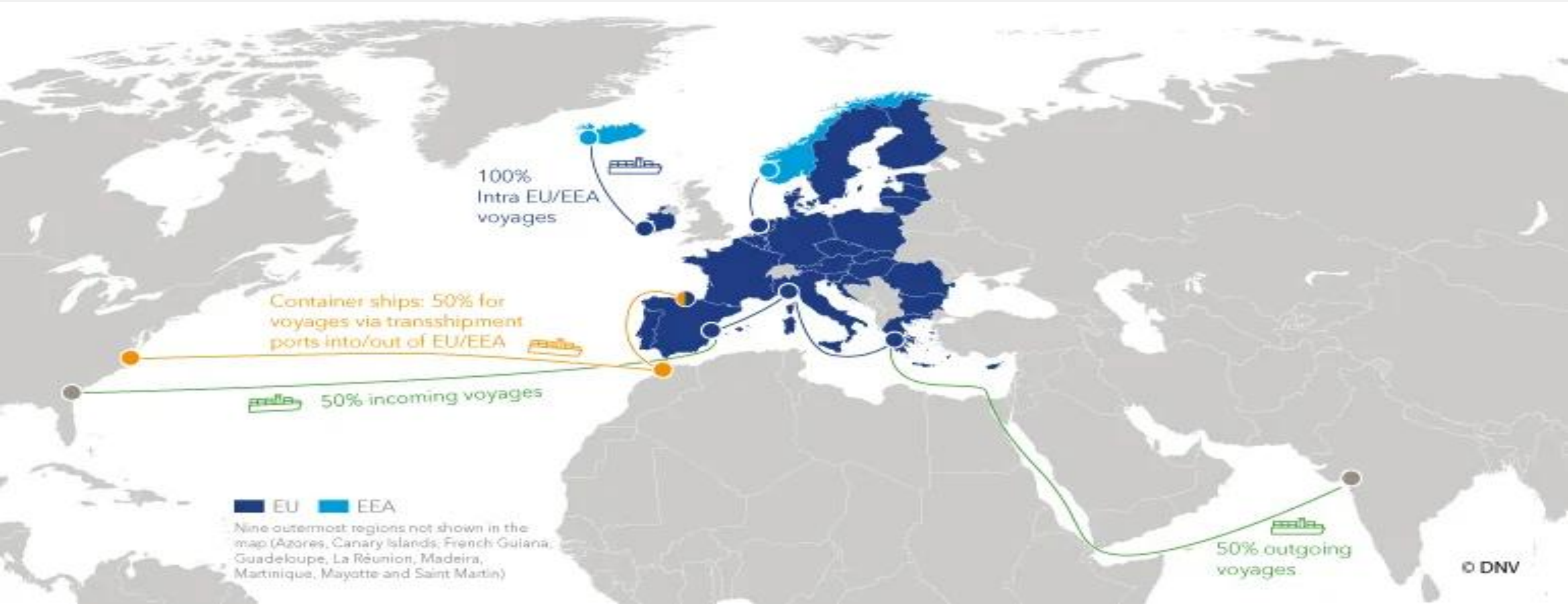
Environmental Impact of Shipping

New Regulatory Framework

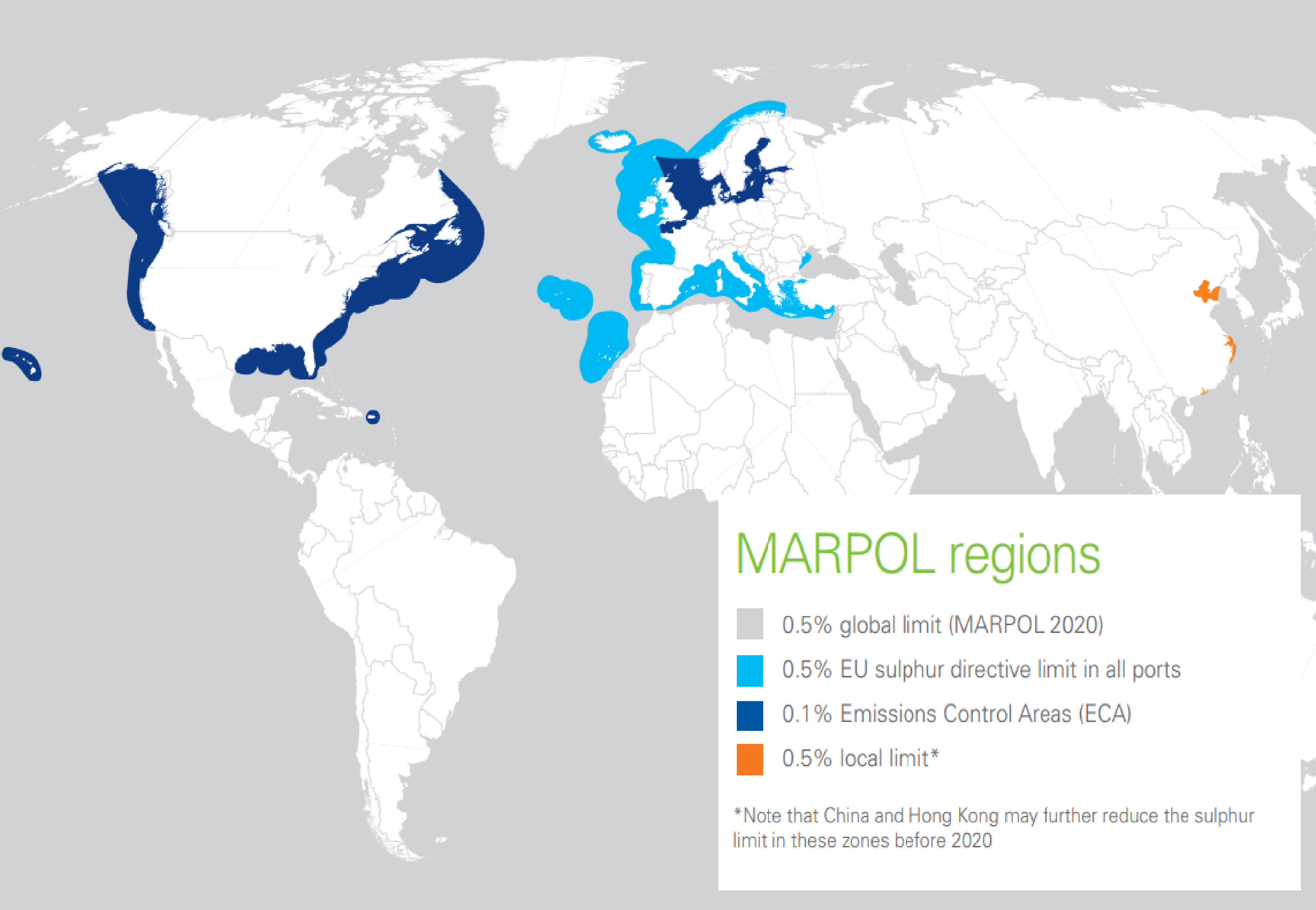
- IMO/Marpol Annex VI
- EU ETS
- Fuel EU
- ECAs

New Energy Mixture Required

- Opportunities & Challenges
- Maritime Sector Credibility
- Cost Reduction
- Impact would be huge

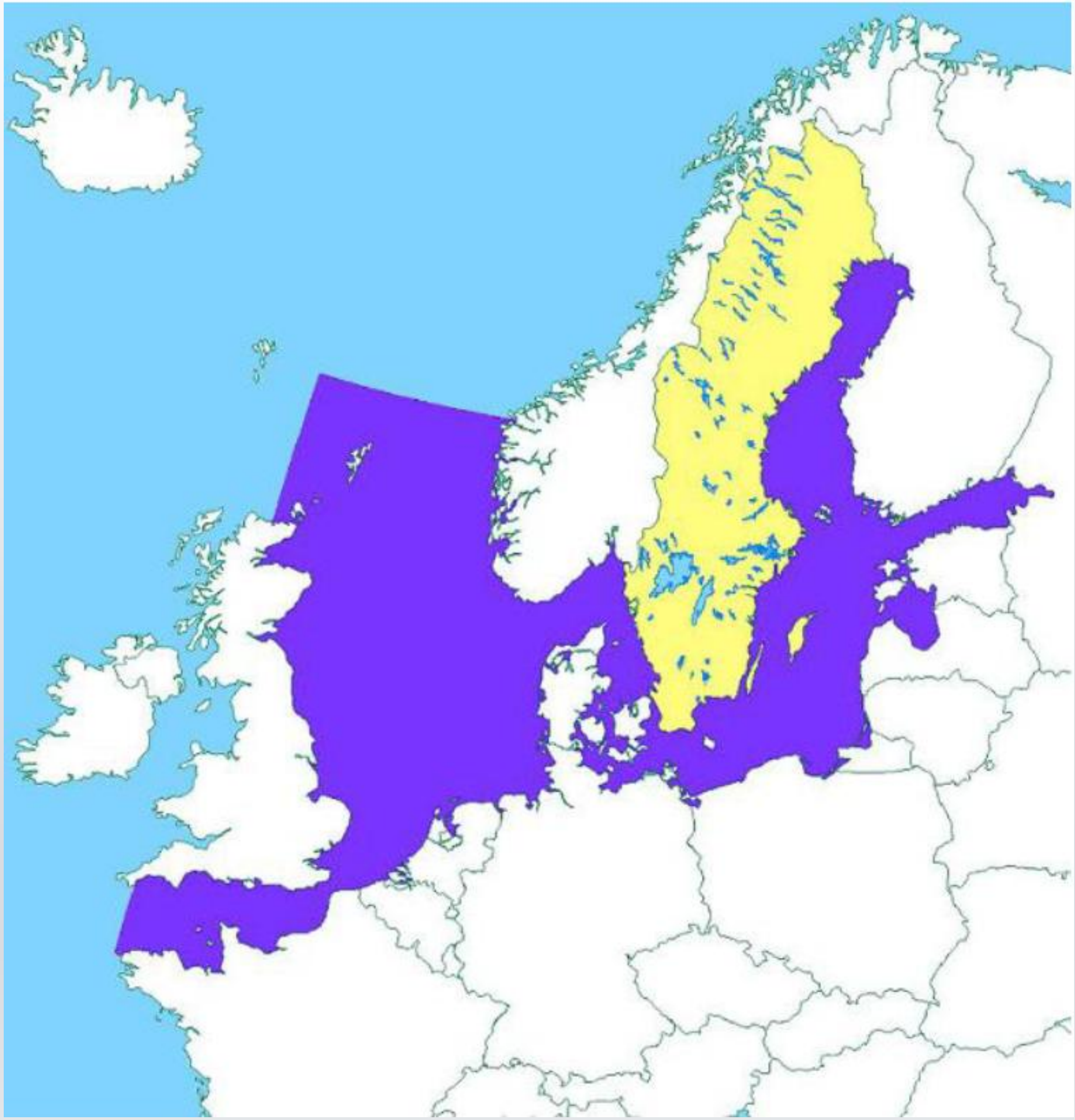


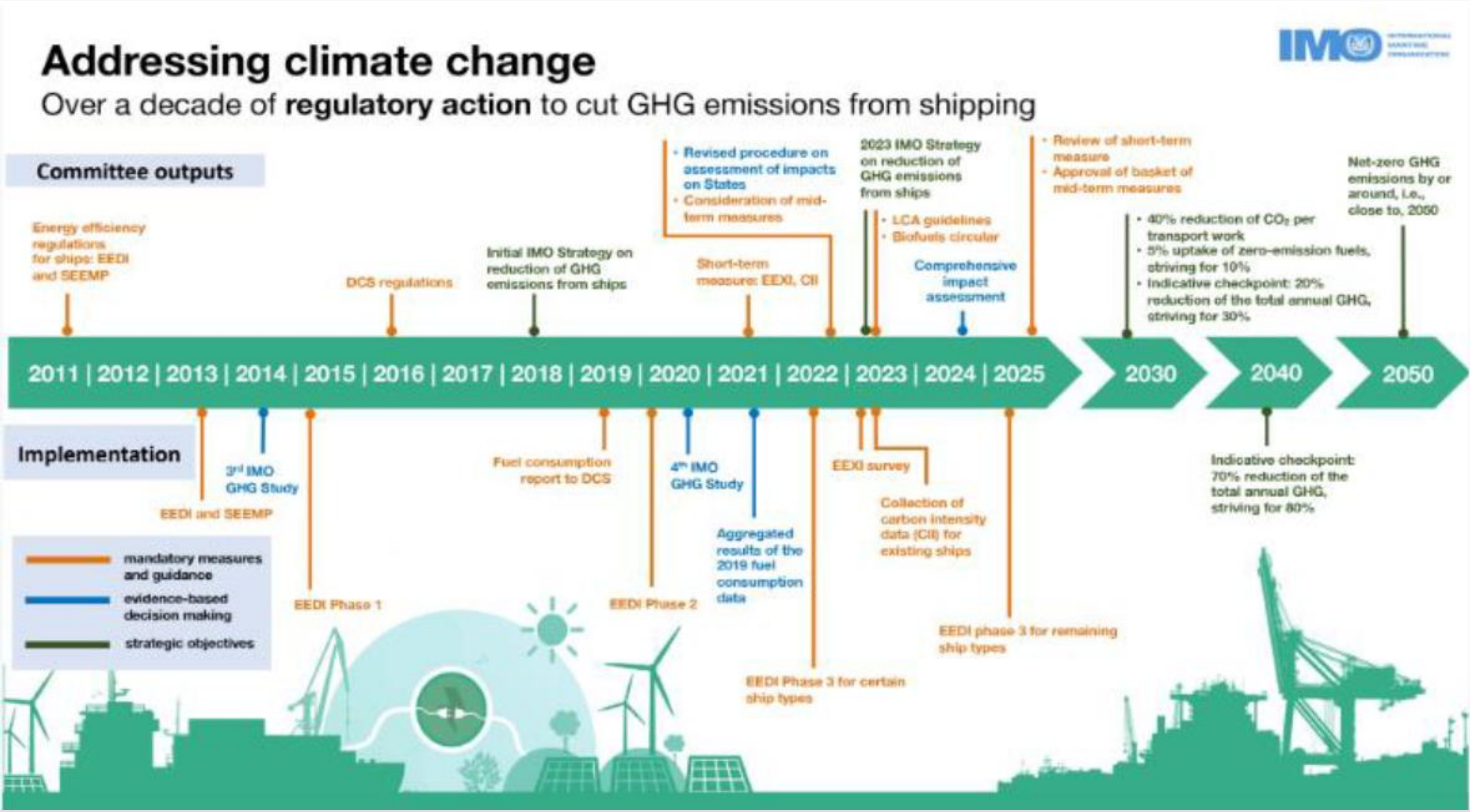
Environmental Impact of Shipping



Baltic and North Sea

Emission Control Areas




Addressing climate change
Over a decade of regulatory action to cut GHG emissions from shipping
Committee outputs
Energy efficiency regulations for ships: EEDI and SEEMP
DCS regulations
Initial IMO Strategy on reduction of GHG emissions from ships
• Revised procedure on assessment of impacts on States
• Consideration of mid-term measures
Short-term measure: EEXI, CII
2023 IMO Strategy on reduction of GHG emissions from ships
• LCA guidelines
• Biofuels circular
Comprehensive impact assessment
• Review of short-term measure
• Approval of basket of mid-term measures
• 40% reduction of CO_2 per transport work
• 5% uptake of zero-emission fuels, striving for 10%
• Indicative checkpoint: 20% reduction of the total annual GHG, striving for 30%
Net-zero GHG emissions by or around, i.e., close to, 2050
2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 | 2023 | 2024 | 2025
2030
2040
2050
Implementation
EEDI and SEEMP
3rd IMO GHG Study
EEDI Phase 1
Fuel consumption report to DCS
EEDI Phase 2
4th IMO GHG Study
Aggregated results of the 2019 fuel consumption data
EEDI Phase 3 for certain ship types
EEXI survey
Collection of carbon intensity data (CII) for existing ships
EEDI phase 3 for remaining ship types
Indicative checkpoint: 70% reduction of the total annual GHG, striving for 80%
mandatory measures and guidance
evidence-based decision making
strategic objectives

Stakeholders

Shipowner

- Cost effective solution
- Safe & Reliable
- Compliant with legislation
- Easy to use
- Easy to store
- Easy to find
- Ships should travel continuously

Ship Services Company

- Reliable Equipment
- Safe & Cost effective
- Compliant with legislation
- Easy to integrate with existing technology
- Profitable solution
- Customer Satisfactions

Port Authorities, Employees, Government, Local Communities, Fishing Sector, Consumers, Fuel Producers, Midstream Suppliers, STS Providers, Environment

Liquid H2, LNG, NH3 and Methanol as Energy Carriers

Liquid Hydrogen

- The Industrial Gases market will rise above $150 billion by 2030
- It has been used for decades in liquid form (NASA space program)
- Established Market but used to be minor, and usages were for special purposes
- Existed Technology can be used
- Variety of Production Methods (SMR, **Electrolysis**, Coal Gasification etc.)
- Highly flammable
- Nontoxic & Non-corrosive
- High energy density by mass (low by volume)
- Hydrogen Embrittlement
- High Burning Velocity
- High Diffusivity
- Cryogenic Liquid (-253degC)
- Volume Shrinks x 850

Liquid H2, LNG, NH3 and Methanol as Energy Carriers

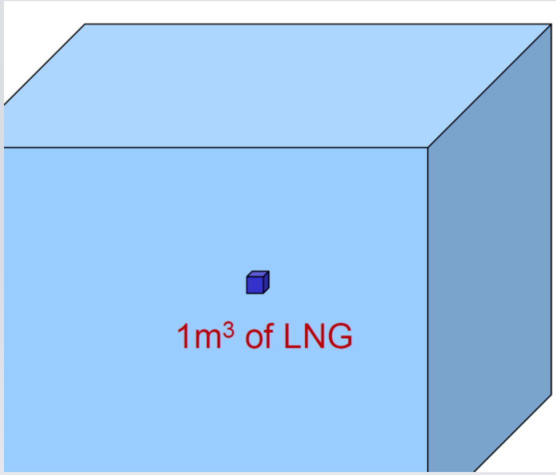
Liquid Hydrogen

- Cryogenic Burns
- Asphyxiation in confined spaces
- During a leakage, vaporization occurs (turns back to gaseous phase)
- Accumulation in ceilings
- Liquefaction needs purification
- Invisible flames and lack of flame sensation
- UV radiation (not IR radiation)-difficult to detect
- Rapid Phase Transition, BLEVE, Vapour Cloud Explosion
- Detonation or Deflagration (1g TNT detonation energy)
- Gas jet, Jet fire etc.
- Hellium (-268degC) is needed for inertization and purging
- Difficult to produce & costly to store it

Liquid H2, LNG, NH3 and Methanol as Energy Carriers

LNG

- Well-established infrastructure & technology
- The LNG market will be rocketed to $65billion by 2030
- A reliable means of transportation, the cleanest fossil fuel (methane 85%-95%)
- Flexible in political turmoil (Ship to Ship Operations)
- Cryogenic Liquid (-162degC)-Cryogenic Burns
- Flammability ranges from 5% to 15% by volume in air
- Autoignition temperature 540deg C
- High energy density per mass and per volume
- Shrinks down to 600 times
- RPT, Vapour Cold Explosion, BLEVE
- Non-toxic and considered less harmful for the aquatic life



Liquid H2, LNG, NH3 and Methanol as Energy Carriers

Liquid H2, LNG, NH3 & Methanol Properties & Hazards

NH3

- Well-established infrastructure & technology
- 150 MT produced in 2022, 90% Haber-Bosch process
- 90% for fertilizers feedstock, the rest for industrial purposes
- New technologies arise (Electrochemical Haber-Bosch Production, Decarbonized Gasification, Green and Blue Refinery Operations, FCC metal looping, Poly)
- Corrosive & Toxic
- Flammability ranges from 15% to 25% in O2
- Autoignition temperature 630degC
- Liquifies at -33degC (anhydrous ammonia)
- Low burning velocity (but under lab conditions, the real world is different)
- It is not easy to be burned directly (environmental impact)
- First NH3 fuel-ready ship delivered in 2022-Ship to Ship operation in Indonesia
- Hundreds of ports across the globe already have the needed transportation infrastructure)

Liquid H2, LNG, NH3 & Methanol Properties & Hazards

Methanol

• Colorless organic liquid at normal Pressures and Temperatures

•Sweet mild odor and taste

•Hygroscopic and completely miscible with water

•Toxic and flammable (6,7% to 36%)

•Burns with low visibility flame

•Very corrosive with metal parts and rubber, gaskets, o rings. Stainless steel is needed for storage

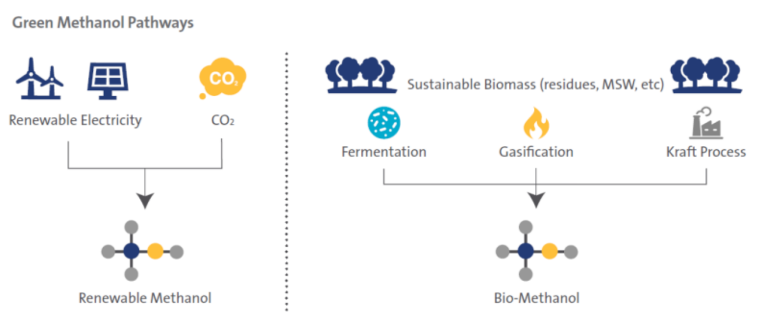
•Heat of combustion 20kJ/g

• It is readily biodegradable in both aerobic and anaerobic environments, with a half-life in surface and groundwater of just one to seven days, compared to a half-life for example of benzene in groundwater of 10-730 days

•Mainly produced by steam reforming of Natural Gas

•Considered a carbon fuel

•Green Methanol pathways



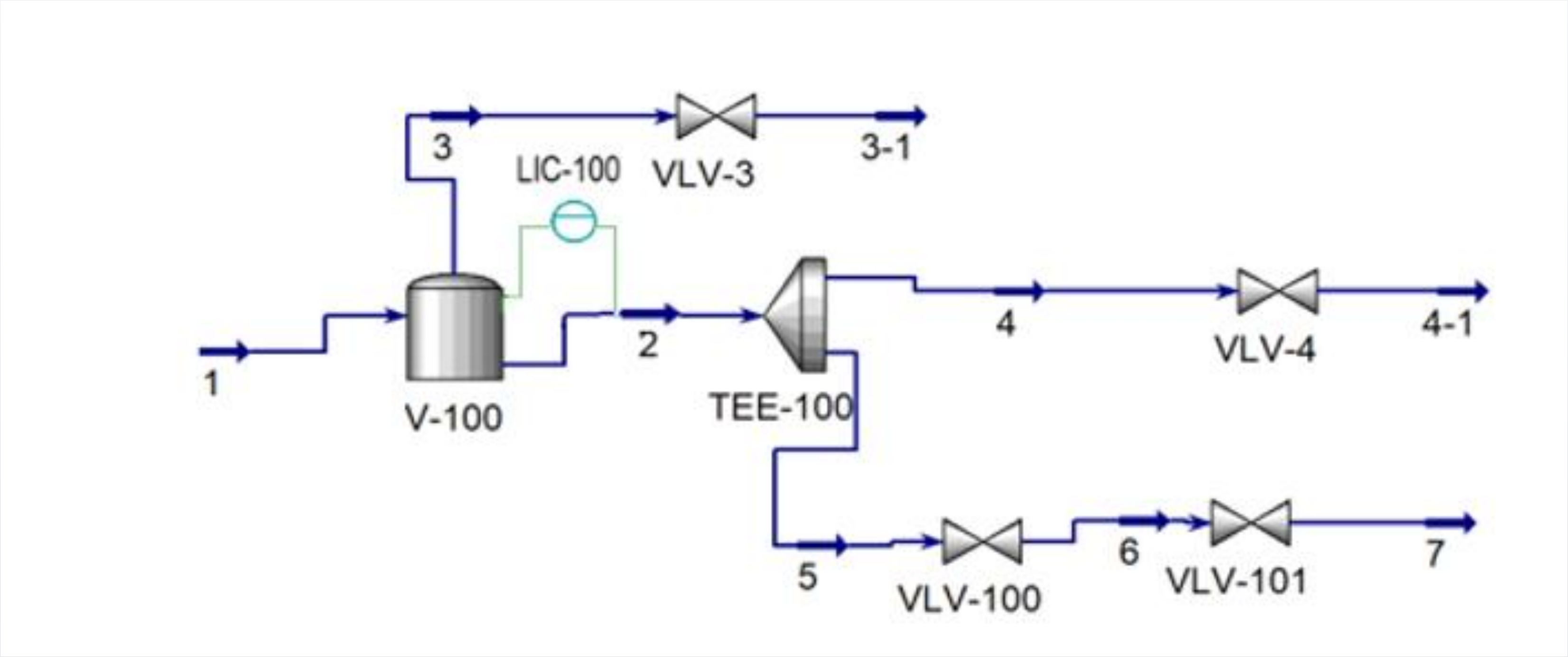
Storage & Trasnportation

Comparison of the Three Gaseous Energy Carriers

- All three energy carriers hide challenges and opportunities
- Efficient Storage will play a key role
- New Transportation Network, Upgrade of the old one
- Hybrid Operations
- Oil & Gas, Industrial Gases, Renewables Industry, Maritime Industry, Logistics
- Safety and Economics will keep the industries reliable & and prosperous
- Smooth Transition
- Many challenges

ASPEN HYSYS Simulation (Version 14)

- A simple system, 100m3 storage tank
- Liquid H2-Anhydrous Liquid NH3-High Methane Content LNG
- Targets: BOG and Leakage Simulation



BOG Simulation of the three energy carriers

ASPEN HYSYS Simulation (Version 14)

- Peng-Robinson Equation
- Steady State Simulation
- 100% pure H2
- Anhydrous Liquid Ammonia
- LNG composition selected

Component	LNG Composition
Methane	96.07
Ethane	2.67
Propane	0.77
n-Butane	0.18
iso-Butane	0.21
Pentane	0.01
Nitrogen	0.01

BOG Simulation of the three energy carriers

ASPEN HYSYS Simulation (Version 14)-Simulation Strategy

- Evaluation of BOG under various pressure and temperature scenarios
- More specifically, investigation of different pressure and temperature scenarios that are likely to occur under marine conditions
- Due to different boiling points, the comparison could not take place straightforward on an absolute temperature scale
- Cryogenic tanks typically reflect pressures as high as 16 bar to reduce extremely low-temperature requirements
- Conversely, Ammonia reflects much lower B.P. at ambient pressure.
- Thus, various tank pressures were applied to evaluate the differences better
- Different BOG rates can be observed in Figures 2,3& 4
- Different BOG rates can be observed in Figures 5,6&7

BOG Results under different pressures

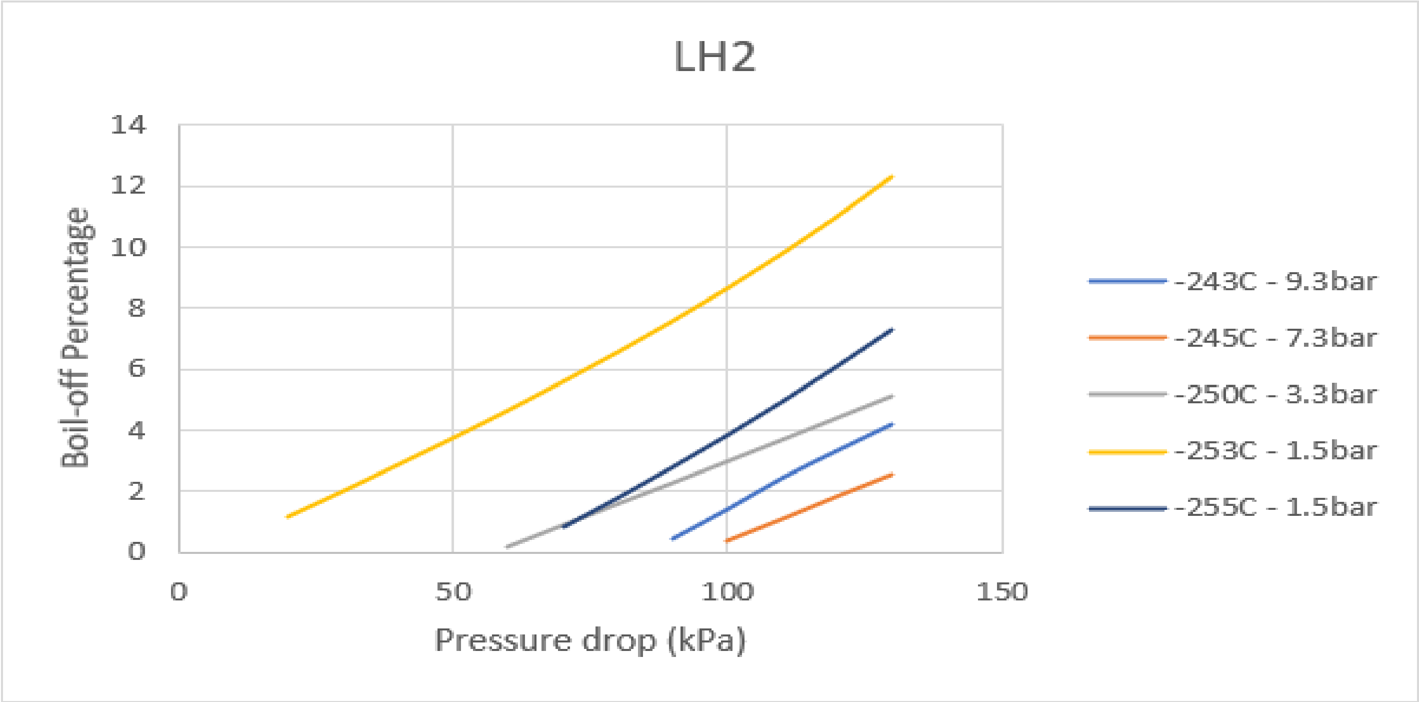


Figure 2. Boil-off percentage of LH2 tank due to pressure variations.

- **Liquid H2** presents higher BOG rates in comparison to the other energy carriers
- Close to its boiling point at -253C and 1.5bar a 100-kPa pressure difference results in evaporation of 8.5% of the tank’s volume.

BOG Results under different pressures

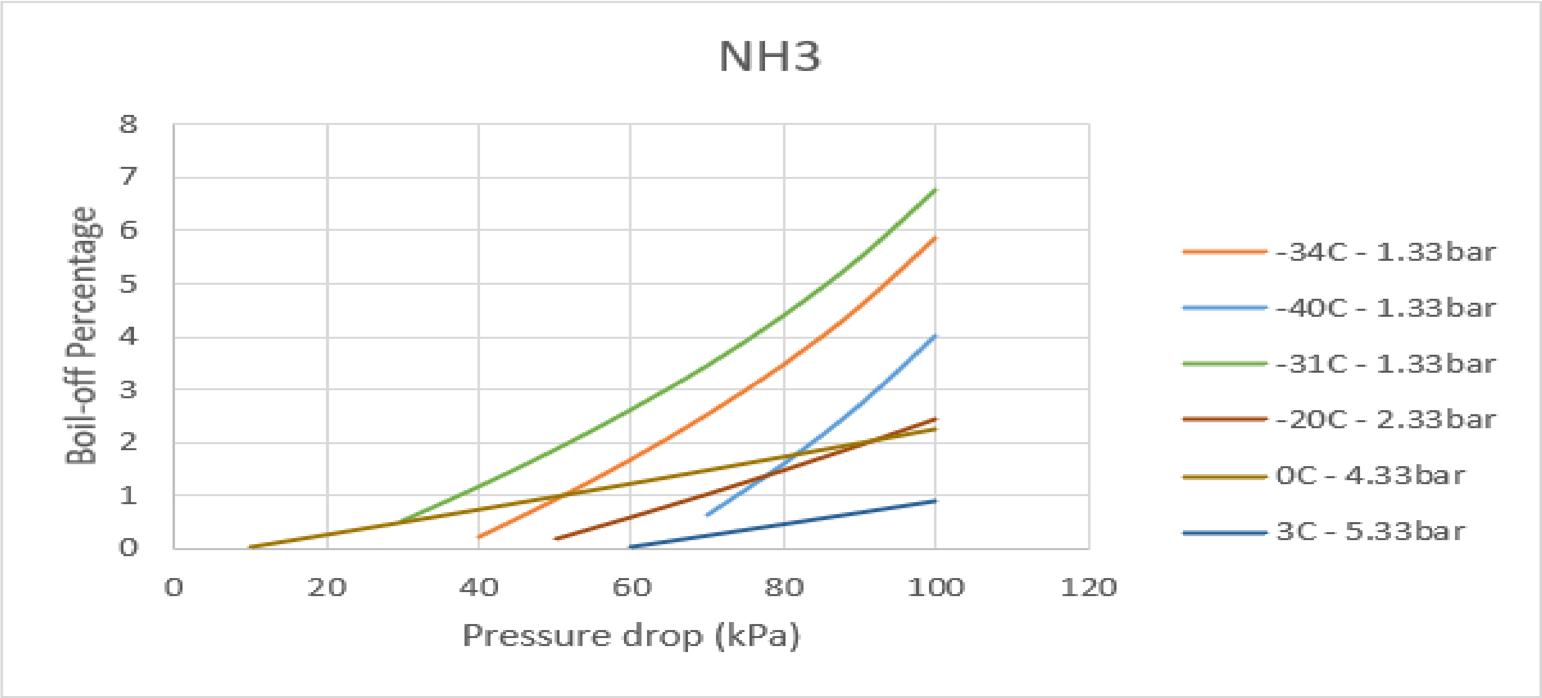


Figure 3. Boil-off percentage of NH3 tank due to pressure variations.

•Conversely, NH_3 near its boiling point at -34C and a smaller tank pressure of 1.33 bar reflects a much lower BOG percentage of 5.9%.

BOG Results under different pressures

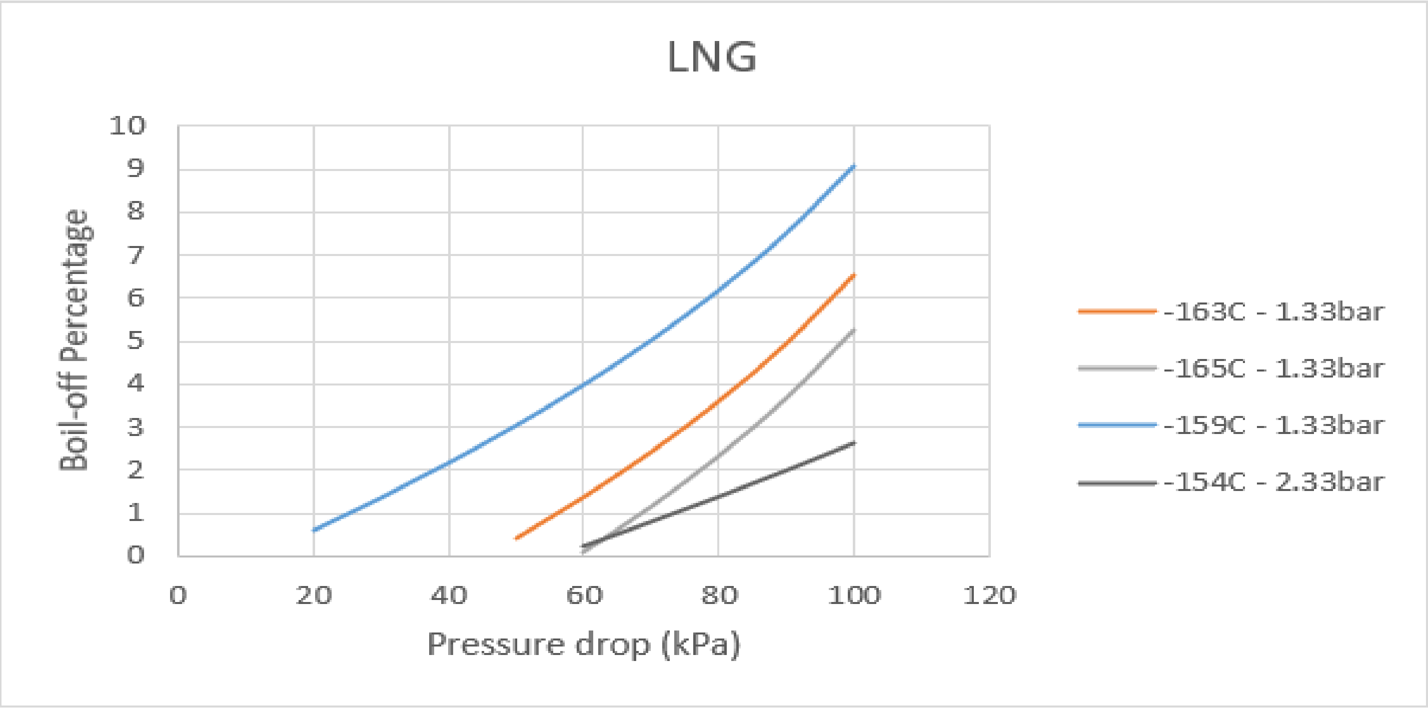


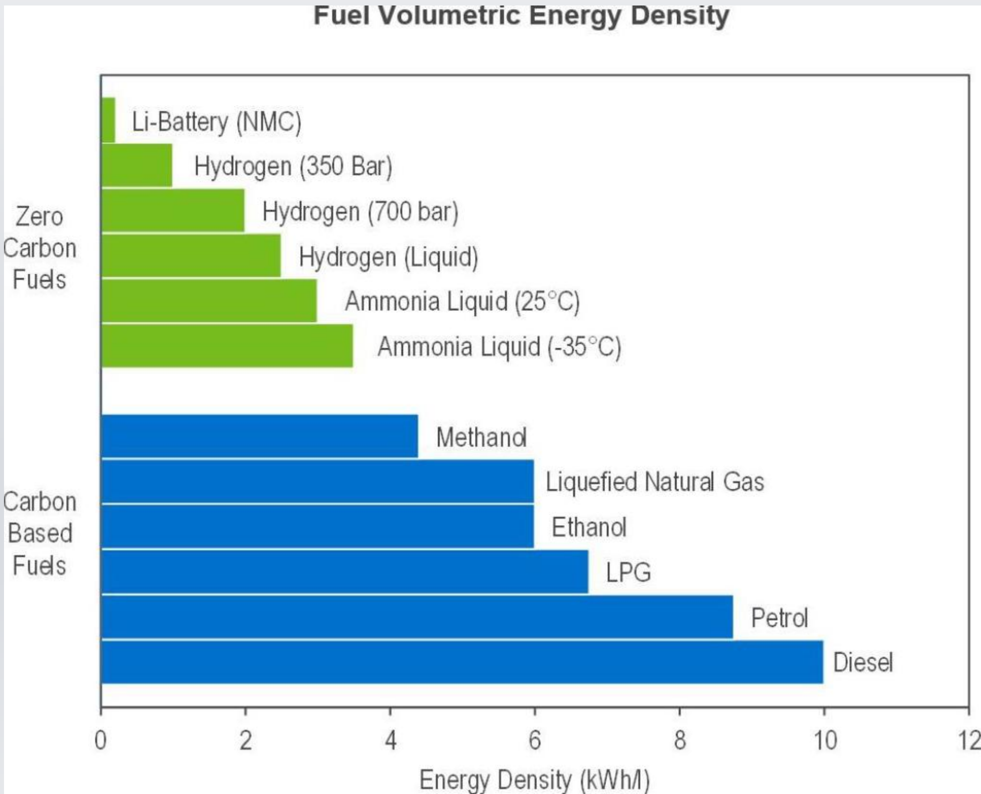
Figure 4. Boil-off percentage of LNG tank due to pressure variations.

•Similarly, **the selected LNG composition** near its boiling temperature of -164degC and the same pressure reflects a boil-off percentage of 6.6%. As the tank pressure increases, the boil-off rate decreases for all three cases; however, the effect is more pronounced for ammonia.

BOG Simulation of the three energy carriers

BOG Results under different pressures

- Hence, **not only milder temperature conditions** are required for the storage and transportation of **NH3**, but most importantly, **higher tank pressures markedly reduce BOG**.



BOG Simulation of the three energy carriers

BOG Results under different temperatures

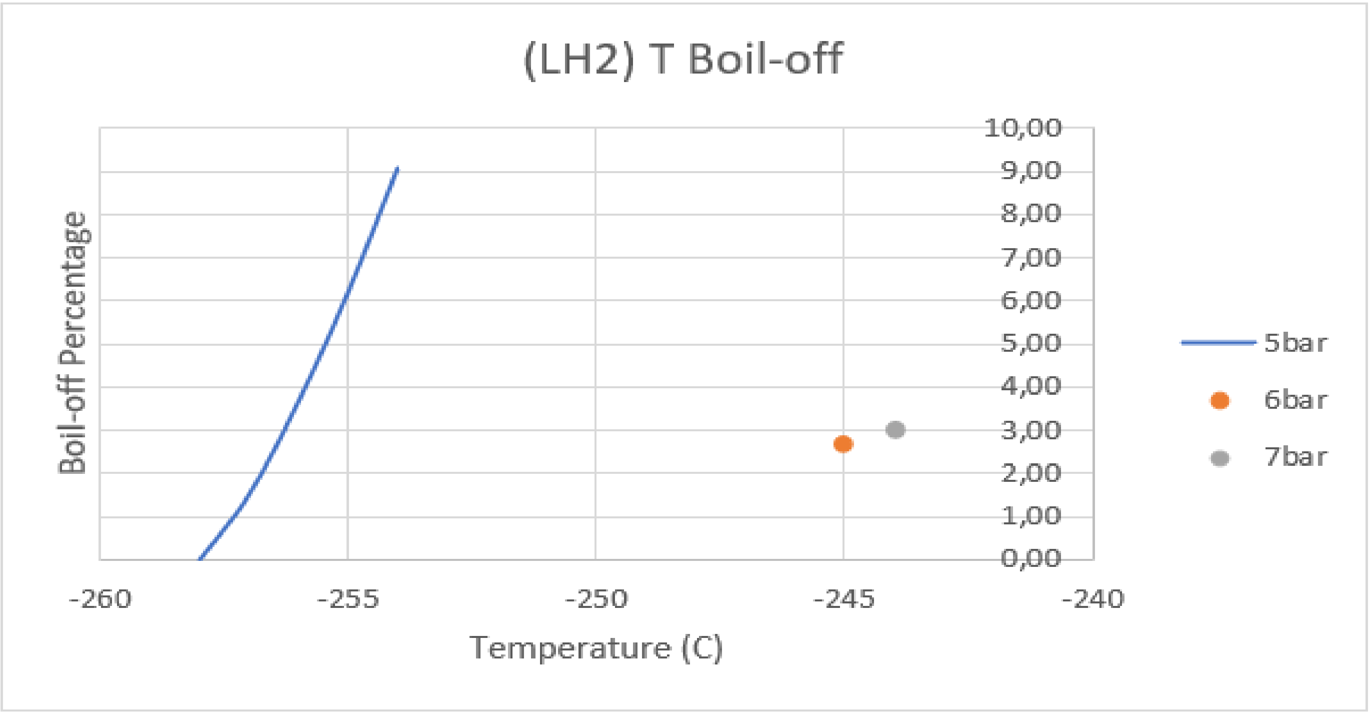


Figure 5. Boil-off percentage of LH2 tank due to temperature variations.

•Temperature variations exhibit a similar trend

•Higher tank pressures (gt 5bar) had to be employed for **H2** to remain in the liquid phase but be that as it may, a temperature drop from -258C to -254C at 5bar led to a boil-off percentage of 9%

BOG Results under different pressures

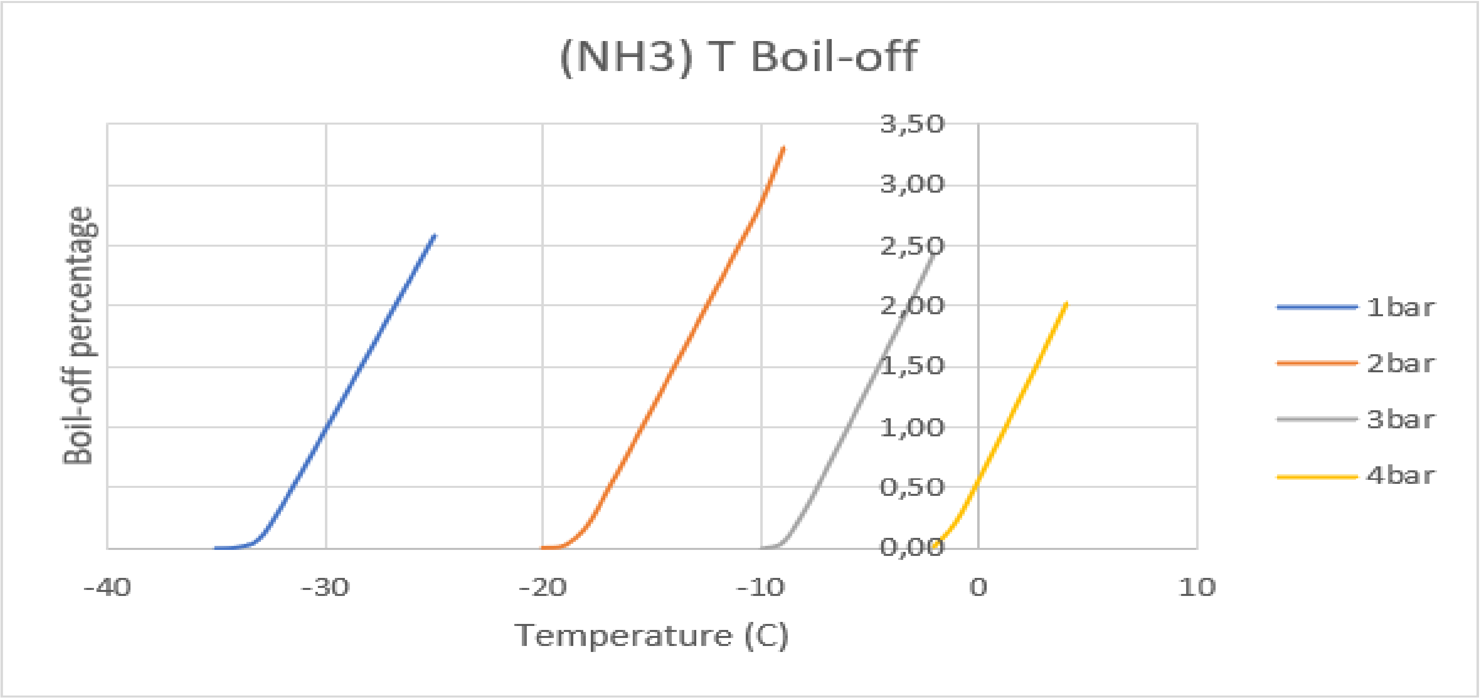


Figure 6. Boil-off percentage of NH3 tank due to temperature variations.

•**NH3**, can be seen that exhibits the lowest BOG percentages due to temperature variations. As for the other cases, increasing the storage pressure has a beneficial effect on the BOG percentage

BOG Results under different pressures

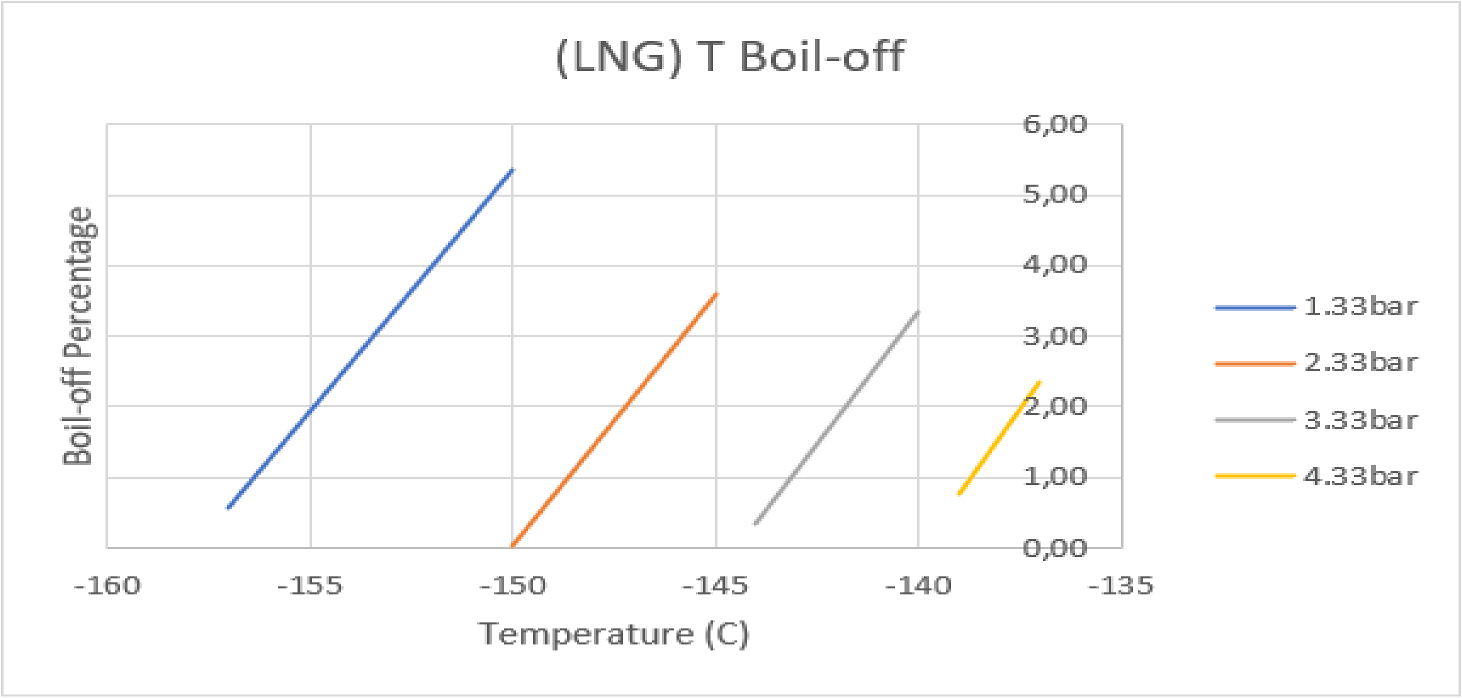
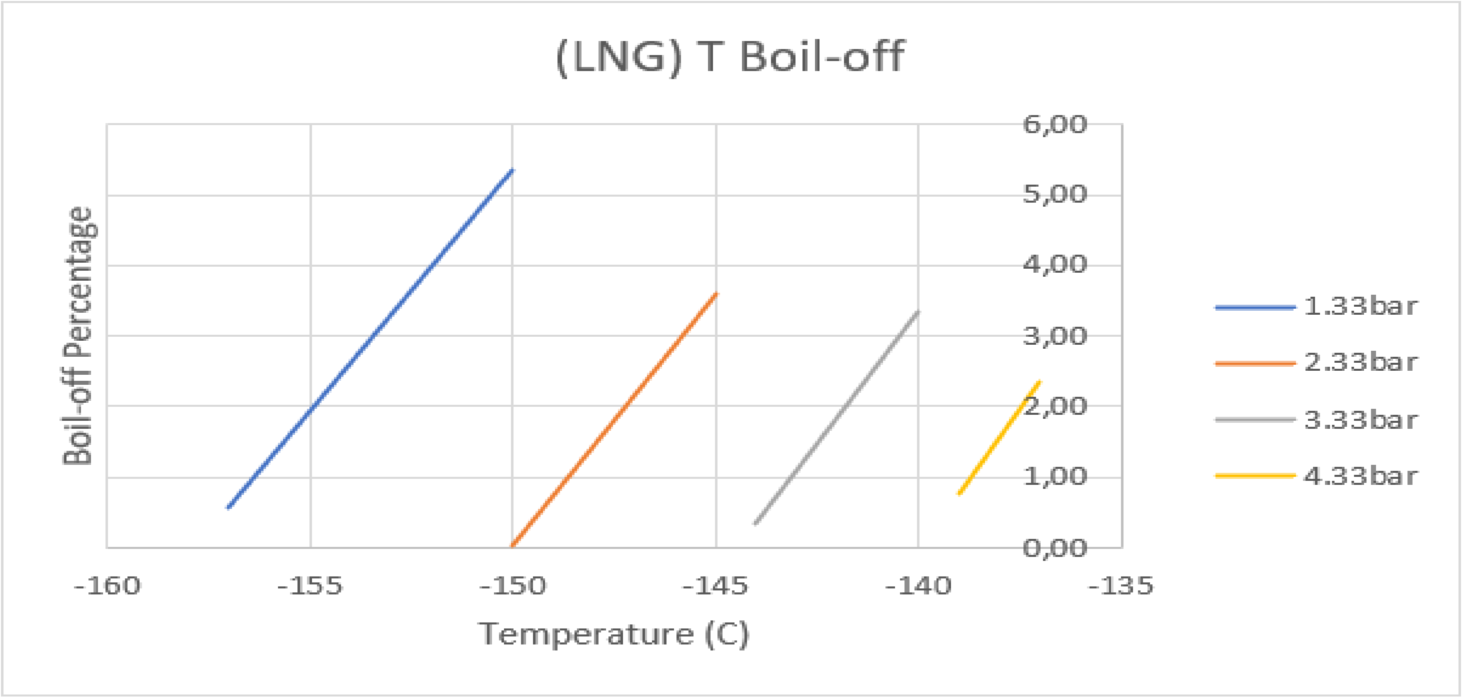


Figure 7. Boil-off percentage of LNG tank due to temperature variations.

•The boil-off rates for **LNG** are significantly lower even at 1bar pressures while increasing the tank pressure leads to reduced the BOG percentage.

BOG Simulation of the three energy carriers

BOG Results under different pressures



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BOG Results under different pressures

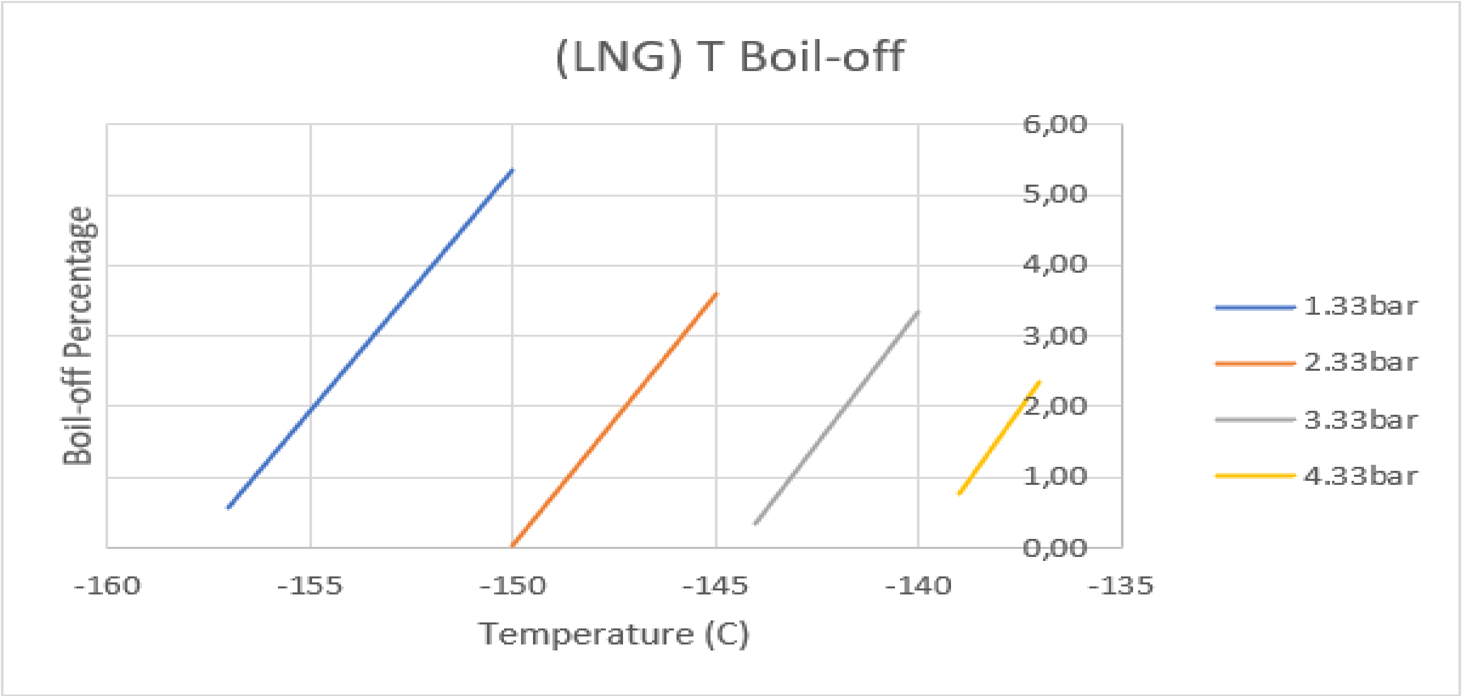
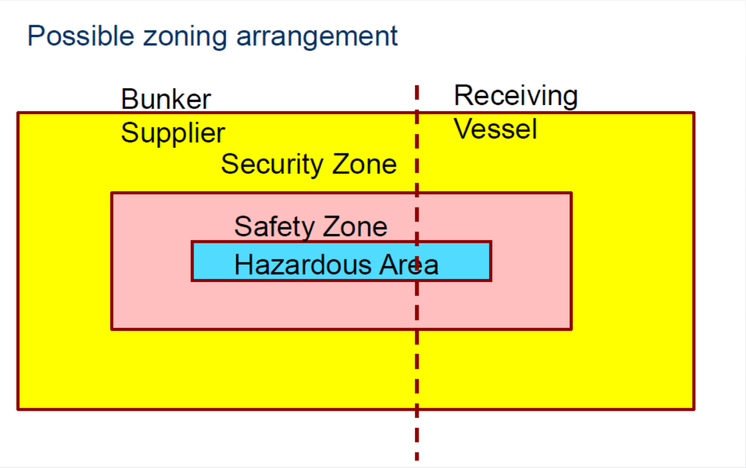


Figure 7. Boil-off percentage of LNG tank due to temperature variations.

•The boil-off rates for **LNG** are significantly lower even at 1bar pressures while increasing the tank pressure leads to reduced the BOG percentage.

BOG Results under different pressures

- Overall, **NH3** poses an economically favorable option with milder temperature requirements, for which higher tank pressures can significantly reduce the, at any rate small boil-off phenomena.



Conclusions & Further Investigation

Conclusions

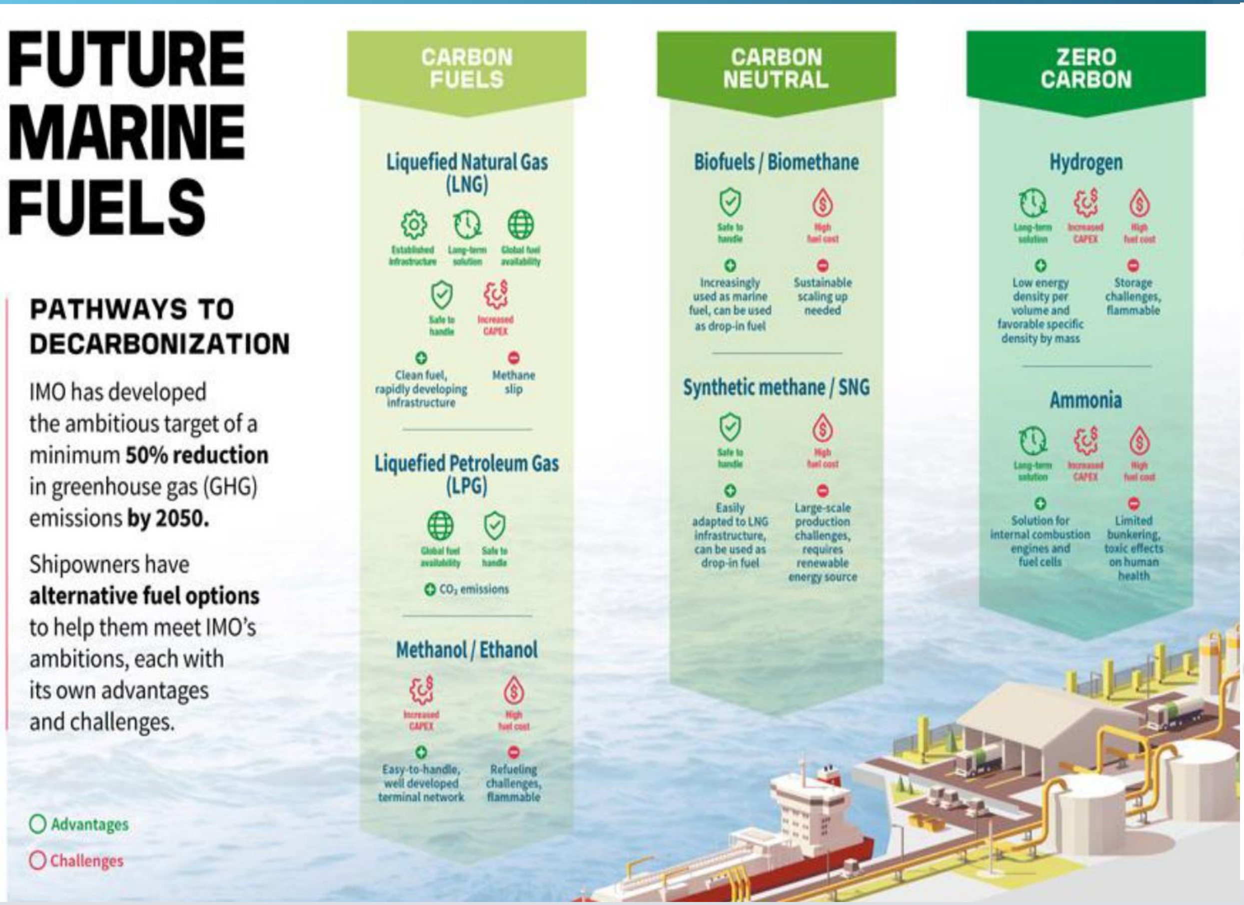
- Storage & and transportation infrastructure maturity levels suggest that **LNG** shall remain the market's working horse for the near future.
- Storage and marine transportation of **liquid hydrogen** requires extreme temperatures and higher pressures with significantly higher BOG losses, which will inevitably increase its associated costs.
- Also, being more susceptible to leakage issues, reflecting a wider flammability ratio with atmospheric air, material compatibility issues, and lack of existing safety network of **global regulations and infrastructure** adds technical constraints.
- Conversely, **NH3** presents a cost-effective candidate, offering mild temperature and pressure conditions for adequate energy transportation, and the lowest BOG losses. Its role as an energy carrier where hydrogen will be the end product is a scenario but must be enviromentaly & and economically evaluated further.

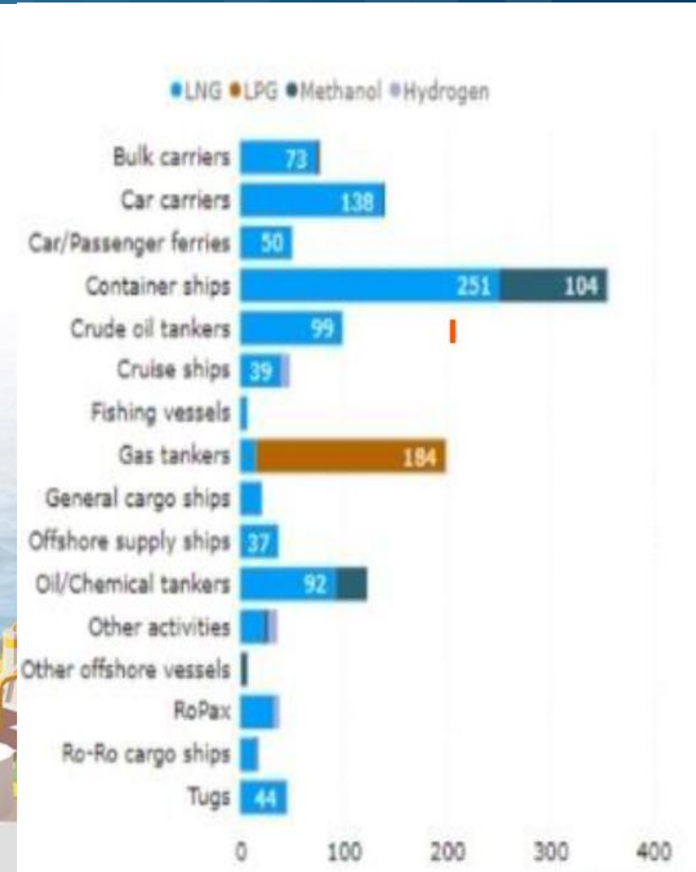
Conclusions & Further Investigation

Conclusions

- Although leakage simulation has been attempted, it was decided that a thorough investigation with a more suitable for such purposes simulation suite is needed.
- ANSYS simulation for leakages, CFD model built & and different system conditions scenarios and parameters could add real value in the future for better qualitative and quantitative assessment.
- All three energy carriers present advantages and disadvantages and it is very important to enhance the creation and the review of safety regulations with global acceptance, so the markets can adjust to the new energy era that has already begun.

Conclusions & Further Investigation





There are currently ~1000 ships using LNG, ~200 using methanol ~2 using H2

Many are becoming NH3 fuel ready

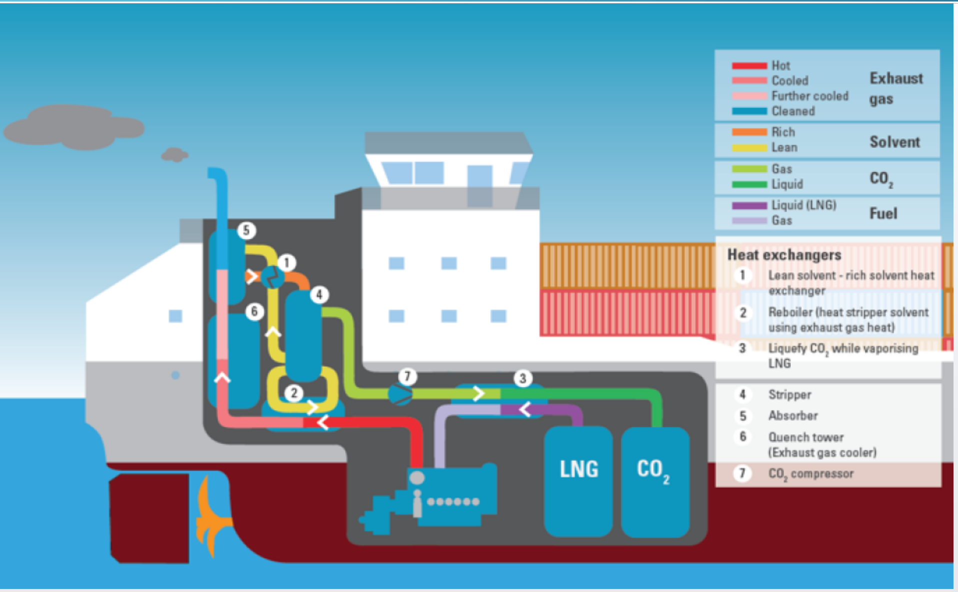
Conclusions

Conclusions

Hybrid Solutions

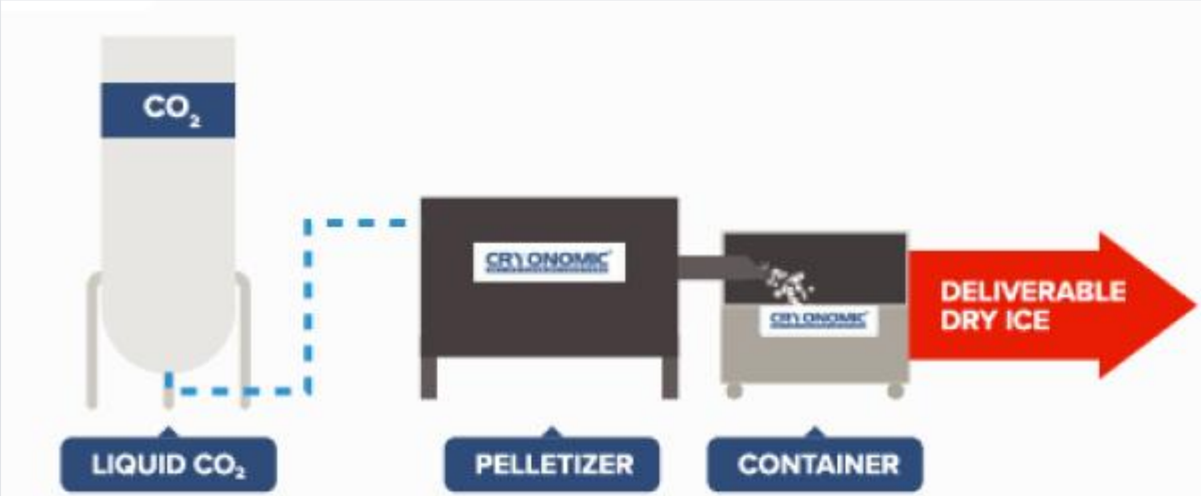
Fransisco High Speed Catamaran

Conclusions



Alternative Fules & CO2 Capture & Utilization

- Hybrid Solutions
- A new market will rise
- Full of Opportunities and Challenges



Conclusions

Hydrogen will play a pivotal role in the energy transition regarding maritime sector, either in its pure form, as part of carbon capture and utilization solutions or as a key component in low-carbon alternatives